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PATENT SPECIFICATION

NO DRAWINGS

L146.668

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COMPLETE SPECIFICATION

Modified Clay

We, IMPERIAL CHEMICAL INDUSTRIES LTD., a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to naturally occurring water-swellaable clays modified by a polymer of vinyl pyrrolidone and to aqueous compositions which contain a modified clay of this type as thickener.

The naturally occurring water-swellaable clays, such as bentonite or hectorite, are commonly used to induce thickening in aqueous compositions. It has been established that the characteristics of these clays may be modified, for example by treatment with a simple electrolyte such as sodium chloride to improve the hydrophilic characteristics of the clay, or by treatment with organic amines having at least 10—12 carbon atoms or by deposition of certain polymers within the clay lattice to confer hydrophobic characteristics on the clay.

According to the present invention we provide a naturally occurring water-swellaable clay of base exchange capacity from 20—120 milliequivalents per 100 gm. of clay which is modified with a polymer of vinyl pyrrolidone as herein defined.

The modified clay has improved hydrophilic characteristics and in particular it has a capacity for thickening aqueous compositions which is greater than that to be expected from a combination of the known separate thickening capacities of the clay and the modifying polymer.

Particularly suitable clays for use in this invention are those hydrophilic clays containing a high proportion of the mineral montmorillonite such as Wyoming bentonite and hectorite and these clays have a base exchange capacity of about 100 milliequivalents per

100 gms. of clay. The swelling properties of these clays may be enhanced when bivalent cations, such as calcium and magnesium, which are present in the clay, are replaced by monovalent cations such as sodium, and the clays useful in this invention include those naturally occurring clays which have had their power of swelling enhanced by activation with certain reagents, such as for example soda ash or sodium chloride.

The polymer of vinyl pyrrolidone may be a homopolymer of vinyl pyrrolidone, or a water-soluble homopolymer of a derivative thereof, or alternatively it may be a water-soluble copolymer of vinyl pyrrolidone or a derivative thereof with a further suitable copolymerisable monomer. Where reference is made in the general disclosure of this specification to a polymer of vinyl pyrrolidone or to polyvinyl pyrrolidone, it should be understood to include such homopolymers or copolymers. Suitable polymers of vinyl pyrrolidone derivatives include the polymers and copolymers of 3 - methyl - N - vinyl - 2 - pyrrolidone, 4 - methyl - N - vinyl - 2 - pyrrolidone or 3,3 - dimethyl - N - vinyl - 2 - pyrrolidone. Suitable monomers with which vinyl pyrrolidone or a derivative may be copolymerised to provide a water-soluble copolymer include, allyl alcohol, methyl vinyl ether, diallyl phthalate, maleic anhydride, vinyl acetate, and acrylic and methacrylic acids and their derivatives. The water-soluble comonomers are preferred and in general it is preferred that the copolymers contain not less than 20% by weight of vinyl pyrrolidone or its water-soluble derivative.

The molecular weight of the polymer of vinyl pyrrolidone is generally within the limits 2,000—3,000,000 but particularly preferred limits are from 10,000—1,000,000.

The relative proportions of clay and the polymer of pyrrolidone employed in the preparation of the modified clay will depend for example, upon the precise natures of the

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clay and the polymer of pyrrolidone and upon the properties required in the modified clay. In general there may be employed from 5%—400% by weight of the polymer of pyrrolidone based on the weight of clay, although it is usually preferred to use from 20%—100% by weight of the polymer of vinyl pyrrolidone.

In the formation of an aqueous dispersion of a hydrophilic clay, such as bentonite, penetration of water into the montmorillonite lattice occurs and the individual clay lamellae separate from one another. The dispersed clay is therefore in the form of finely divided particles with a very high surface area.

The pyrrolidone rings which are present in the polymers and copolymers of vinyl pyrrolidone, possess electron-donating properties and are readily adsorbed on to solid surfaces or finely divided particles. While the exact mechanism of interaction of a hydrophilic clay and a polymer of vinyl pyrrolidone is not understood, it is believed to involve association of the pyrrolidone ring and the clay surface. Since this association is not a stoichiometric reaction, the relative proportions of polymer and clay may be varied within wide limits.

Since the polymer of vinyl pyrrolidone is completely water-soluble, the preparation of the modified clay is readily conducted in aqueous dispersion. For example, an aqueous dispersion of the clay is prepared and the polymer of an aqueous solution thereof is added to the dispersion. It is an advantage that in the preparation of the dispersion of the clay, prior to the addition of the polymer, the clay may be purified by gravity separation of the siliceous impurities which are commonly present.

As already indicated, the modified clays of this invention are particularly useful as thickeners for aqueous compositions which may contain materials which are in solution and/or in dispersion.

Thus according to a further feature of this invention we provide a thickened aqueous composition which contains as thickener a naturally occurring water swellable clay of base exchange capacity from 20 to 120 milliequivalents per 100 gm. of clay, which is modified with a polymer of vinyl pyrrolidone as herein defined.

Aqueous solutions or dispersions which may be thickened include the solutions of dispersions of inorganic and organic materials which are employed as pharmaceuticals, cosmetics, or in agriculture, or horticulture. For example thickened aqueous agricultural or horticultural compositions may be useful as nematocides, insecticides, fungicides, herbicides, fertilisers, growth regulators and molluscicides.

The thickened aqueous compositions thus obtained exhibit characteristics which are not obtained by the use of the clay or polymer alone. In particular the combination of clay

and polymer in the modified clay of this invention displays a synergistic effect and provides a thickened aqueous composition even when the amounts of clay and polymer, if present separately, would confer little or no thickening. Useful characteristics of the thickened aqueous compositions are the increased viscosities and yield values which result from the use of a given amount of clay. Other useful characteristics of the thickened aqueous compositions are their stability during storage and to any increase of temperature, and their ability to retard the settling out of suspended solid components and the separation of liquid and solid phases of a mixture.

The proportion of modified clay employed in thickening an aqueous composition will depend for example, upon the nature of the modified clay, the nature of the aqueous composition and the degree of thickening required. In general there is employed from 0.25%—10% of clay which is modified with 0.025%—10% of the polymer of vinyl pyrrolidone, both percentages being by weight of the aqueous phase to be thickened.

It is especially preferred to employ from 0.5%—4% by weight of clay based on the aqueous phase to be thickened which is modified with from 0.25%—5% by weight of the polymer based on the aqueous phase. The optimum relative proportions of clay and polymer within these limits are best determined by experiment for the particular system in which the thickening is required.

Although the modified clays of this invention are of particular value in thickening aqueous solutions and dispersions, they may also be of value in other applications where the polymer modification confers suitable characteristics. Examples of other applications include the stabilisation of emulsions and the preparation of clay films of use, for example, in the encapsulation of medicinals.

The invention is illustrated by the following Examples, in which parts and percentages are by weight.

EXAMPLE I.

This Example illustrates the preparation of an adduct of a Wyoming bentonite having a high montmorillonite content, with polyvinyl pyrrolidone having an average molecular weight of approximately 40,000. 28 parts of Wyoming bentonite were dispersed by shaking in 700 parts of distilled water and the resulting free-flowing suspension was decanted from gritty impurities. To 100 parts of this suspension was added 1.0 part of an aqueous solution of polyvinyl pyrrolidone (commercially available under the Registered Trade Mark 'LUVISKOL' K30), the solution having a polymer content of 38.2%. On stirring the suspension it was converted to a smooth paste. A portion of this paste was evaporated to dryness at 110° C. and the solid

bentonite-polyvinyl pyrrolidone adduct was powdered. The product was dispersible in water.

EXAMPLE II.

- 5 The procedure of Example I was repeated using 5.0 parts of the polyvinyl pyrrolidone solution in place of 1.0 part. A free-flowing dispersion of the bentonite-polymer adduct was formed which was paler in colour than the unmodified clay. A sample of the solid adduct was obtained by evaporation of the dispersion to dryness at 110° C.

EXAMPLE III.

- 15 This Example illustrates the preparation of a polyvinyl pyrrolidone adduct of a purified naturally occurring magnesium aluminium silicate clay (commercially available under the Registered Trade Mark 'VEEGUM HV').
- 20 2.4 parts of purified magnesium aluminium silicate were dispersed in 57.6 parts of distilled water and the dispersion was diluted to a concentration of 2% by addition of a further 60 parts of water. 3.0 parts of a 20% aqueous solution of polyvinyl pyrrolidone having an average molecular weight of approximately 700,000 (commercially available under the registered Trade Mark 'LUVISKOL' K90) were added and mixed
- 30 thoroughly with the suspension of magnesium aluminium silicate. The product was a paste in which the silicate particles appeared to be loosely flocculated.

EXAMPLE IV.

- 35 The procedure of Example III was repeated using 1.0 part of the 38.2% aqueous solution of the polyvinyl pyrrolidone used in Example I, in place of the 3.0 parts of polyvinyl pyrrolidone of Example III. The aqueous product was a smooth paste. On drying a sample of this product at 110° C., it formed

a flexible film and the solid product dispersed when placed in water.

EXAMPLE V.

This Example illustrates the preparation of thickened aqueous compositions which contain a water-swellable clay and polyvinyl pyrrolidone and the existence of an optimum level of polymer modification of the clay for a maximum thickening effect in the composition.

20 parts of a purified naturally occurring magnesium aluminium silicate clay (commercially available under the Registered Trade Mark 'VEEGUM T') were dispersed in 980 parts of hot water by stirring and the resulting free-flowing colloidal dispersion containing 2% by weight of clay was cooled. To separate portions, each of 160 parts, of this dispersion were added various amounts of a 20% solids solution of a polyvinyl pyrrolidone of molecular weight approximately 700,000 (commercially available under the Registered Trade Mark 'LUVISKOL' K90) such that in each, the concentration of the polymer was between 0.25% and 8.0% by weight of the dispersion. Spontaneous gelation of each of the dispersions occurred, the greatest thickening of the composition being achieved when the level of polymer modification of the clay was 2%—3% based on the weight of the aqueous phase.

Quantitative estimates of the consistency of the compositions were made by determining the flow curves expressing shear stress as a function of shear rate of the compositions with an Epprecht-Rheomat "15" rotational viscometer, manufactured by Contraves, A.G., Zurich, and deducing the yield values by extrapolation to zero shear rate. The following results were obtained.

Percentage modification of clay by polyvinyl pyrrolidone based on the aqueous phase	—	0.25	0.5	1.0	2.0	3.0	4.0	5.0	8.0	%
Yield value of polymer modified composition containing 2% of clay	0	80	225	570	775	785	565	340	235	dyne/cm. ²

EXAMPLE VI.

- 85 30 parts of the purified naturally occurring magnesium aluminium silicate clay of Example V were dispersed in 970 parts of hot

water to form a slightly thickened composition having a yield value of 50 dyne/cm.² measured as described in Example V. To separate portions, each of 160 parts, of this dispersion

- were added various amounts of a 38.2% solution of polyvinyl pyrrolidone of molecular weight approximately 40,000 (commercially available under the Registered Trade Mark 'LUVISKOL' K30) such that in each case the concentration of the polymer was between 0.5% and 2.0% by weight of the dispersion. The method of Example V was then used to investigate the consistency of the composition as a function of the level of modification with the following results:

Percentage modification of clay by polyvinyl pyrrolidone based on the aqueous phase	0	0.5	0.75	1.0	1.25	1.5	2.0	%
Yield value of polymer modified composition containing 3% clay	50	93	267	600	265	47	34	dynes/cm. ²

EXAMPLE VII.

- 15 15 parts of a beneficiated hectorite clay (commercially available under the Registered Trade Mark 'MACALOID') was dispersed by stirring in 485 parts of hot distilled water, to give a fluid dispersion of the clay. 100 parts of the dispersion were taken and 2 parts of a solution containing 40% by weight of polyvinyl pyrrolidone of approximate molecular weight 45,000 (commercially available as grade K30-35 from the British Oxygen Company Limited) were added. The mixture 20 formed a semi-rigid composition with a smooth texture. The yield value, measured as described in Example V, was 351 dynes/cm.². There was little change in the consistency of the composition on standing for three days at a temperature of 20° C.—25° C.

EXAMPLE VIII.

- 30 30 parts of a Wyoming bentonite clay were dispersed in 470 parts of distilled water to give a free-flowing dispersion of the clay which was decanted from settled gritty impurities. To 100 parts of this clay suspension were added 3.3 parts of a 17.6% solids aqueous solution of polyvinyl pyrrolidone having a mean molecular weight of 718,000. 40 The dispersion was converted to a stiff semi-rigid composition.

EXAMPLE IX.

- 45 A clay dispersion similar to that of Example VII was prepared using 15 parts of a purified magnesium montmorillonite clay (commercially available under the Registered Trade Mark 'BEN-A-GEL EW') and 485 parts of water. 1.0 part of a 45% solids aqueous solution of polyvinyl pyrrolidone of approximate molecular weight 350,000 (commercially available under the Registered

Trade Mark 'ANTARA K60') was added to 100 parts of the clay dispersion. The composition became stiff and semi-rigid and had a yield value of 726 dynes/cm.², measured as described in Example V. 55

EXAMPLE X.

100 parts of the aqueous dispersion of Wyoming bentonite clay of Example VIII were taken and 2.46 parts of a 50% solids isopropanol solution of a water-soluble 30/70 copolymer of vinyl pyrrolidone/vinyl acetate of molecular weight approximately 30,000 (commercially available under the Registered Trade Mark 'ANTARA I-335') were added with stirring. The bentonite dispersion became semi-rigid with a yield value of 118 dynes/cm.², measured as described in Example V. 60 65

EXAMPLE XI.

The procedure of Example X was repeated using 2.27 parts of a 50% solids isopropanol solution of a water-soluble 70/30 vinyl pyrrolidone/vinyl acetate copolymer of molecular weight approximately 60,000 (commercially available under the Registered Trade Mark 'ANTARA I-735') in place of 2.46 parts of the solution employed in Example X. A very stiff composition was formed. 70 75

EXAMPLE XII.

This Example illustrates the use of the present invention to prevent settling of an inorganic solid in aqueous dispersion. A 20% aqueous dispersion of a purified naturally occurring magnesium aluminium silicate clay was prepared using the method of Example V. To 160 parts of this dispersion were added 16 parts of the 20% aqueous solution of polyvinyl pyrrolidone of Example V. 100 parts of the resulting thickened composition were taken and 5 parts of powdered titanium 80 85 90

dioxide were added with stirring. A homogeneous composition was formed in which the titanium dioxide showed no tendency to settle out on standing.

5 WHAT WE CLAIM IS:—

1. A naturally occurring water swellable clay of base exchange capacity from 20 to 120 milliequivalents per 100 gms. of clay which is modified with a polymer of vinyl pyrrolidone as herein defined.

10 2. A modified clay as claimed in Claim 1 wherein the polymer of vinyl pyrrolidone has a molecular weight of from 10,000 to 1,000,000.

15 3. A modified clay as claimed in Claim 1 or Claim 2 wherein the clay is modified with from 5% to 400% by weight of the polymer of vinyl pyrrolidone based on the weight of the clay.

20 4. A modified clay as claimed in Claim 3 wherein the clay is modified with from 20% to 100% by weight of the polymer of vinyl pyrrolidone based on the weight of the clay.

25 5. A modified clay substantially as herein described and with reference to the foregoing Examples.

6. A thickened aqueous composition which contains as thickener a naturally occurring water swellable clay of base exchange capacity from 20—120 milliequivalents per 100 gms. of clay which is modified with a polymer of vinyl pyrrolidone as herein defined. 30

7. A thickened aqueous composition as claimed in Claim 6 wherein there is employed from 0.25% to 10% by weight of the unmodified clay based on the weight of the aqueous phase of the composition, said clay being modified with from 0.025% to 10% by weight of the polymer of vinyl pyrrolidone based on the weight of the aqueous phase of the composition. 35 40

8. A thickened aqueous composition as claimed in Claim 7 wherein there is employed from 0.5% to 4% by weight of the unmodified clay, said clay being modified with from 0.25% to 5% by weight of the polymer of vinyl pyrrolidone. 45

9. A thickened aqueous composition substantially as herein described with reference to the foregoing examples. 50

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